California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE ANALYSIS OF AUTOMOTIVE EXHAUST FOR METHANOL AND ETHANOL

Standard Operating Procedure No. MLD 101
Revision 2.2

January 2005

Southern Laboratory Branch
Monitoring and Laboratory Division
9528 Telstar Avenue
El Monte, CA 91731

SOP No. 101 - PROCEDURE FOR THE ANALYSIS OF AUTOMOTIVE EXHAUST FOR METHANOL AND ETHANOL

1 Introduction

1.1 This document describes a method of analyzing automotive exhaust for methanol and ethanol in the range of 1 to 1200 micrograms (µg) per 15 milliliter (mL) of solution. Other alcohols soluble in water may also be determined should peak identification and calibrations are performed.

1.2 This procedure is based on a method developed by the U.S. Environmental Protection Agency (EPA, Ref. 9.1) which involves sampling diluted engine exhaust through deionized water contained in glass impingers and analyzing this solution by gas chromatography. This method does not encompass sample collection procedures.

1.3 This SOP is based on Method 1001 of the California Non-methane Organic Gas Test Procedures Part C, *California Air Resources Board*, Amended July 30, 2002

1.4 High concentrations may be determined by quantitatively diluting the aqueous solution with deionized water.

2 Method Summary

2.1 The samples, typically a pair of a primary and a back-up impingers, are received.

2.2 The sample is introduced into a gas chromatograph (GC) by a liquid autosampler. The alcohols in the sample are separated in a GC capillary column and subsequently detected and quantified by a flame ionization detector (FID).

3 Interferences and Limitations

3.1 An interferent is any component present in the sample with a retention time similar to that of any target alcohol described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method or instrumentation, e.g., GC/MS.

3.2 The concentration of the alcohols in the range of interest is stable for up to six days as long as the samples are sealed and refrigerated at a temperature below 40 ºF. Therefore, samples must be kept refrigerated and be analyzed within six days of sampling.

4 Instrumentation and Apparatus

4.1 The analytical system is comprised of the following:

4.1.1 Gas chromatograph (GC), Varian model CP3800 or equivalent, equipped with DB-Wax Megabore column [30 meters, 0.53 millimeters (mm) internal diameter (ID), 1 micron (µ) film thickness] and flame ionization detector (FID). Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy, and resolution of all the target compounds.

4.1.2 Autosampler, Varian model CP8400 or equivalent. This model is capable of keeping the sample cool with a refrigerated, re-circulating water bath. Refrigeration is not required. The CP3800 may also be used without refrigeration.

4.1.3 Varian Star version 6.0 data system or equivalent.

5 Reagents and Materials

5.1 Methanol, 99.9%, HPLC grade, EM Science or equivalent.

5.2 Ethanol, absolute, ACS reagent grade.

5.3 ASTM Type I purified water, HPLC grade, Burdick and Jackson or equivalent, or ASTM Type II deionized water.

5.4 Stock solutions are prepared by diluting approximately 1 g (must be weighed with an analytical balance capable of readability of 0.1 mg) each of methanol and ethanol with high purity water to the mark of a 100.0 mL flask. The concentrations of these standards are calculated and expressed in µg /mL.

5.4.1 Stock solutions must be prepared at least every six months.

5.4.2 Calibration standards are prepared by successive dilutions of the stock solution(s). A typical calibration standard is 3.0 µg /mL, though higher concentration standards should be used for high concentration samples. Figure 1 illustrates typical chromatograms of a methanol/ethanol standard. Calibration standards must be replaced at least every week.

5.4.3 A control standard is also prepared by successive dilutions of a stock solution different from that of the calibration standard. The concentration should be approximately that of the samples, typically 1.5 µg /mL. Control standards must be replaced at least every week.

5.4.4 Standards used for linearity and LOD determinations (Section 8) are also prepared by successive dilutions of an appropriate level stock solution.

5.4.5 All standards should be refrigerated at a temperature below 40 ^{o}F during storage.

5.5 If other alcohols are found in the exhaust, standards containing these additional compounds are prepared, as above.

5.6 Gas requirements:

5.6.1 Air shall be “Zero” grade (<1 ppmC total hydrocarbon contamination) or better.

5.6.2 Nitrogen shall have a minimum purity of 99.998 percent.

5.6.3 Helium shall have a minimum purity of 99.995 percent.

5.6.4 Hydrogen shall have a minimum purity of 99.995 percent.

6 Procedure

6.1 After sampling, the solution is either analyzed immediately or stored at a temperature below 40 ^{o}F.

6.2 Prior to analysis, an aliquot of 1 to 2 mL of each sample is transferred to a 2-mL autosampler vial and allowed to warm to approximately 15 ^{o}C, if using a refrigerated autosampler.

6.3 If using an unrefrigerated autosampler, the vials are allowed to warm to room temperature prior to analysis.

6.4 A 1.0 microliter aliquot of each unmodified sample is injected via autosampler into a gas chromatograph, configured to operate under the following nominal conditions:

Column	DB-wax, 30 m, 0.53 mm ID, 1.0 µ film thickness
Carrier gas	helium at 5 mL/minute (mL/min)
Make-up gas	nitrogen at 25 mL/min
Detector	FID, hydrogen at 30 mL/min, air at 300 mL/min; 275^{o}C
Injector	on-column injection; 150^{o}C
Autosampler temperature (if applicable)	15^{o}C
Temperature	50^{o}C (hold 1 min), 50^{o}C to 65^{o}C (5^{o}C/min, hold 0.5 min), 65^{o}C to 110^{o}C (15^{o}C/min), 110^{o}C (hold 3.5 min)

6.5 Samples containing compounds having concentrations above the documented range of instrument linearity must be diluted and reanalyzed.

6.6 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

6.7 The peak identifications provided by the computer are checked and corrected if necessary.

6.8 The above procedure may be modified for analysis of higher alcohols by increasing the final temperature and adjusting the temperature ramping to achieve good separation of the desired components.

7 Calculations

7.1 The concentration of each alcohol is determined by comparing the sample peak area with that of an external standard:

$$Concentration\left(\mu g/mL\right)_{Sample} = PeakArea_{Sample} * ResponseFactor$$

where the response factor (RF) is calculated during the calibration by:

$$RF = \frac{Concentration_{Standard}\left(\mu g/mL\right)}{Peak\ Area_{Standard}}$$

7.2 This concentration is then used to calculate the total amount of methanol and ethanol in each impinger:

$$Mass\left(\mu g\right) = Concentration\left(\mu g/mL\right) * Impinger\ Volume$$

7.2.1 The impinger volume is 15 mL.

8 Quality Control

8.1 Blank Runs

8.1.1 A deionized water blank is run each analysis day to check the water used for sampling and the analytical system for contamination.

8.1.2 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the blank analysis is repeated.

8.1.3 If the peak area is consistent, the blank value is subtracted from the samples. (Note: The standards should be prepared with water containing no alcohol.)

8.1.4 If the peak area is not consistent, the source of the contamination must be investigated.

8.1.5 A trip blank is also analyzed for every emission test.

8.1.6 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the blank value is subtracted from the samples.

8.2 Calibration Run: A single-point calibration is performed for each analysis day. The sample load frequently requires continuous instrument operation into the next calendar day. In these instances, the calibration factor of the previous calendar day is used for all of the samples of such a sample load.

8.2.1 A response factor for each target alcohol is generated daily by entering the concentration and measured peak area for each alcohol. Figure 2 demonstrates a typical calibration standard chart.

8.2.2 A running mean response factor and standard deviation for each alcohol is calculated and used for the criteria of a calibration standard check.

8.2.3 The instrument or the conditions of the analysis need to be investigated if the measured response factor is outside 3 standard deviation or 10 % from current mean response factor, whichever is greater.

8.2.4 If major problems are discovered or the cause of the failure is unknown, samples should not be analyzed by the GC

8.2.5 Instrument maintenance and repairs can affect the instrument response. If the response changes sufficiently that the subsequent calibration fails the control limits, a new QC chart should be started

8.2.6 In the event that twenty successful calibration analyses have not been performed before the need for running samples, the calibration is considered valid if the control standard run (Section 8.3) passes.

8.3 Control Standard Run: The quality control standard is analyzed at the beginning of each set of samples, repeated approximately every ten samples, and after the last sample.

8.3.1 Obtain at least 20 control standard results to create a control chart and establish control limits. Figure 3 demonstrates a typical set of control standard QC charts.

8.3.2 Calculate the control standard mean from the ratio of the measured value to the theoretical value for each target alcohol.

8.3.3 Calculate the control standard deviation from the ratio of the measured value to the theoretical value for each target alcohol.

8.3.4 Establish an upper and lower warming limits at either two standard deviations or 5 percent, whichever is greater, above and below the mean ratio. A measured ratio outside of this limit is considered a QC warning. When warnings occur on two consecutive analyses, the second analysis is considered a QC failure.

8.3.5 Establish an upper and lower QC control limits at either three standard deviations or 5 percent, whichever is greater, above and below the mean ratio. A measured ratio outside this limit is considered a QC failure.

8.3.6 In the event that twenty successful control standard analyses have not been performed before the need for running samples, an alternative QC criterion will be used. In this case, a measured concentration greater than 10% from the theoretical concentration is considered a QC failure.

8.3.7 A QC failure requires that the instrument and the conditions of analysis be investigated before running samples. If major problems are discovered or the cause of the failure is unknown, samples should not be analyzed by the GC. Any sample analyses performed are considered invalid.

8.4 Replicate Run: A replicate analysis performed on one of approximately every 10 samples, or at least once per analysis day. The relative percent difference (RPD) in concentration between the pair of analyses is calculated for each of the target alcohols and compared to an allowable limit. A sample replicate chart is shown in Figure 4.

8.4.1 The RPD is calculated as follows:

$$RPD = \frac{|Sample\ Conc. - Replicate\ Conc.|}{Average\ Conc. of\ Both\ Analyses} \times 100$$

8.4.2 A limit on the allowable RPD is established based on the average concentration of the replicate runs, as shown in the following table:

Average Measurement for Replicate Runs	Allowable RPD (%)
1 to 10 times LOD	100
10 to 20 times LOD	30
20 to 50 times LOD	20
Greater than 50 times LOD	15

8.4.3 If the measured RPD of any of the target compounds is greater than the allowable limit, the sample should be analyzed again. If reanalysis is not feasible or if the RPD criteria are still not met on reanalysis, all of the sample results for that analysis day from the instrument are considered invalid.

8.5 Linearity Determination: A multipoint calibration of each of the target alcohols is performed to confirm instrument linearity. This is done for new instruments, after making instrument modifications which can affect linearity, and at least once per year.

8.5.1 The multipoint calibration consists of analyses of at least five concentration levels of standards distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis based on the 'least squares' method is performed using concentration as the independent variable and peak area as the dependent variable to determine a correlation coefficient (r). The r must be greater than 0.995 for the method to be considered sufficiently linear to ensure the validity of using a single-point calibration for daily analysis.

8.6 LOD Determination: A limit of detection (LOD) determination for each of the target alcohols is performed for new instruments, after making modifications which can affect the sensitivity of an instrument, and at least once per year. Figure 5 shows a typical LOD determination.

8.6.1 LOD determination consists of analyses of at least four "low" concentration levels standards, each above the LOD, with at least five replicate determinations of the lowest concentration standard.

8.6.2 The LOD determination can be performed concurrently with the linearity determination (Section 8.5) if at least five replicate measurements of the lowest concentration level standard are performed.

8.6.3 The concentration of the lowest standard must be greater than the calculated laboratory LOD, and not more than five times the estimated LOD.

8.6.4 A linear regression analysis is performed on this data set to identify slopes, m_i, for each of the *i*th target alcohols.

8.6.5 For each of the *i*th target compounds, the standard deviations, s_i, in units of peak area are determined using the five (or more) replicate measurements of the lowest concentration standard. These are then converted to units of concentration using the slopes determined in Section 8.6.1.

$$s_i^{conc} = \frac{s_i^{area}}{m_i}$$

8.6.6 The LOD for each of the *i*th target compounds can now be calculated using the following equation:

$$LOD_i = t * s_i^{conc}$$

where *t* is the Student's *t* value associated with a 98% confidence interval.

8.6.7 The Student's *t* value is dependent upon the degrees of freedom associated with the analysis. The degrees of freedom of the analysis is equal to the number of replicate measurements, n, of the lowest concentration standard minus one. An abbreviated table of values of t associated with a 98% confidence interval is shown below (Ref. 9.2):

Degrees of Freedom (n-1)	t-value
4	3.7
5	3.4
6	3.1
7	3.0

8.6.8 The maximum allowable LOD for each compound is 0.10 μg/mL. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD for sample analyses to be considered valid.

8.6.9 For sample analysis, all peaks identified as target compounds that are equal to or greater than the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, SLB may set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.6.10 For the purpose of calculating the total mass of all species, the concentrations of all compounds below the LOD are considered to be zero.

9 References

9.1 "EPA Method Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles", EPA 460/3-82-004, U.S. Environmental Protection Agency.

9.2 Harris, Daniel C., "Quantitative Chemical Analysis", *W.H. Freeman & Co*., 4th ed., 1995.

10 Revision History

S.O.P. No. MLD 101, Revision 2.1, April 2001

S.O.P. No. MLD 101, Revision 2.0, September 1, 1996

S.O.P. No. MLD 101, Revision 1.1, July 1993

S.O.P. No. MLD 101, Revision 1.0, November 1, 1989

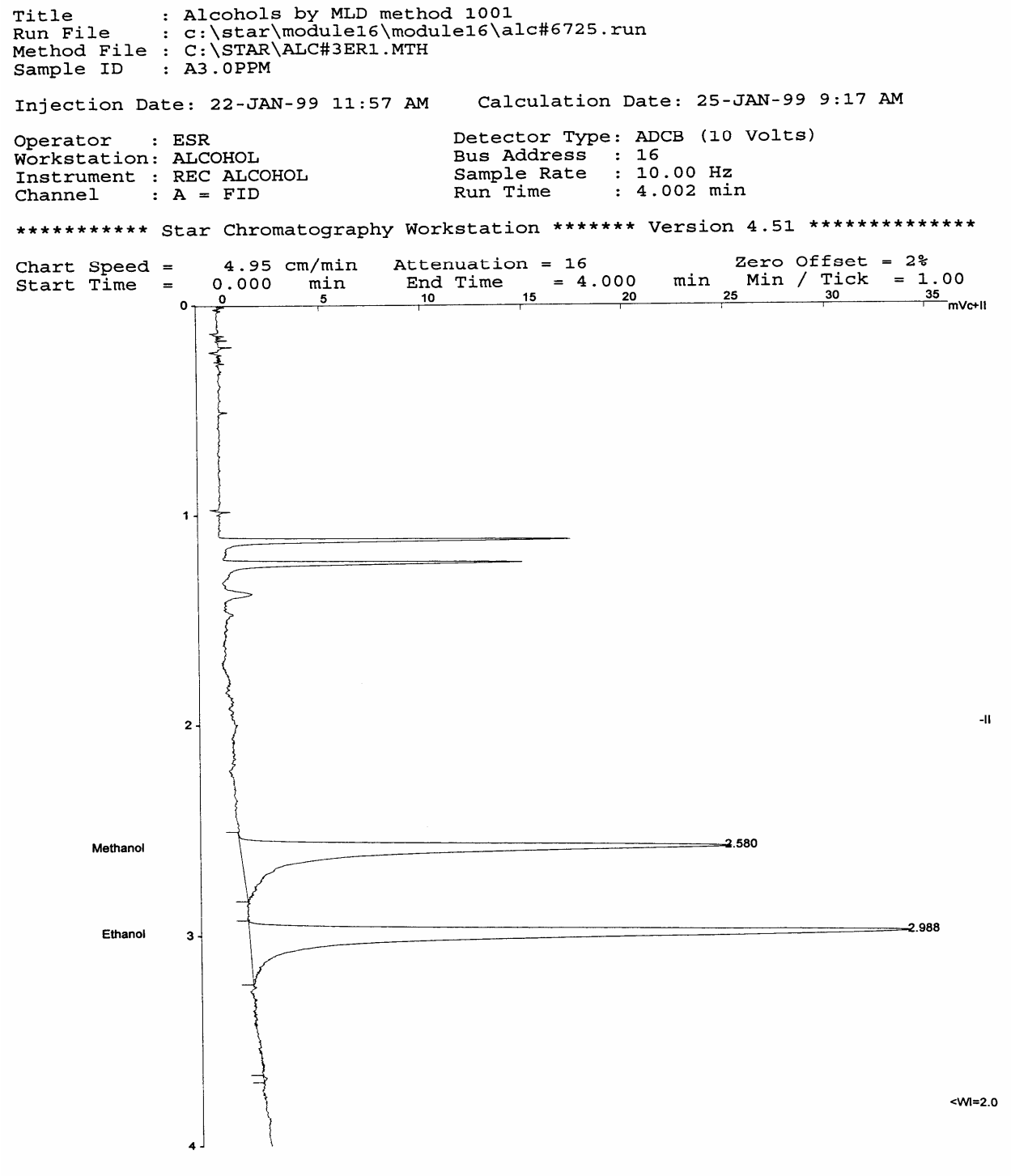


Figure 1. Calibration Standard Chromatogram

DATE OF ALC ANAL.	AREA COUNT	CALIBRATION FACTOR	STATUS	VALID DATA	AVERAGE	STDEV.	% Diff.	CONC.
5/12/04	11443	3779	OK	3779	3721	184	1.6%	3.028
5/13/04	11567	3820	OK	3820	3723	182	2.6%	3.028
5/14/04	11396	3764	OK	3764	3724	181	1.1%	3.028
5/17/04	10945	3615	OK	3615	3722	179	-2.9%	3.028
5/25/04	11798	3924	OK	3924	3726	180	5.3%	3.007
5/26/04	11233	3736	OK	3736	3726	178	0.3%	3.007
5/27/04	11226	3733	OK	3733	3726	176	0.2%	3.007
5/28/04	10996	3657	OK	3657	3725	175	-1.8%	3.007
6/3/04	11241	3657	OK	3657	3724	173	-1.8%	3.074
6/4/04	11169	3633	OK	3633	3722	172	-2.4%	3.074
6/7/04	11227	3652	OK	3652	3721	171	-1.8%	3.074
6/8/04	11258	3662	OK	3662	3720	169	-1.5%	3.074
6/9/04	11193	3641	OK	3641	3718	168	-2.1%	3.074
6/14/04	11454	3680	OK	3680	3717	166	-1.0%	3.113
6/15/04	11401	3663	OK	3663	3717	165	-1.5%	3.113
6/16/04	11580	3720	OK	3720	3717	164	0.1%	3.113
6/17/04	11549	3757	OK	3757	3717	162	1.1%	3.074
6/18/04	11716	3811	OK	3811	3719	161	2.5%	3.074
6/23/04	11454	3716	OK	3716	3719	160	-0.1%	3.083
6/24/04	11324	3673	OK	3673	3718	159	-1.2%	3.083

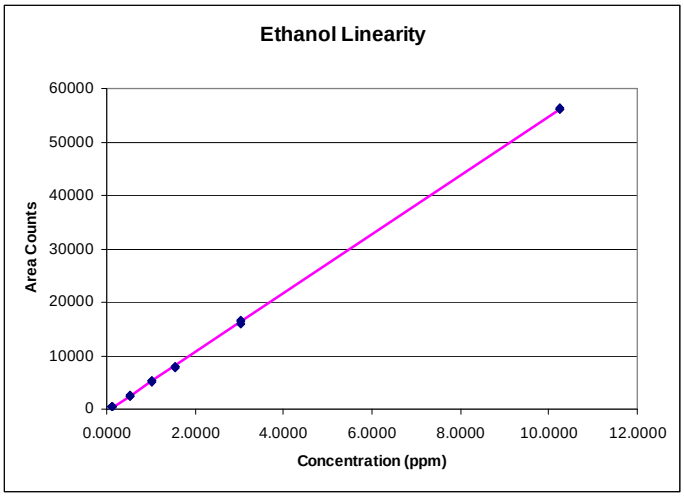
Figure 2. Calibration Standard Quality Control Chart for Methanol

Date of Analysis	Theor. ug/mL	Actual ug/mL	Actual/Theor.	Aver.	Std Dev	Status
10/04/04	1.512	1.496	0.99	1.00	0.04	PASS
	1.512	1.456	0.96	1.00	0.04	PASS
11/16/04	1.564	1.607	1.03	1.00	0.04	PASS
	1.564	1.593	1.02	1.00	0.04	PASS
11/17/04	1.469	1.487	1.01	1.00	0.04	PASS
	1.469	1.556	1.06	1.00	0.04	PASS
11/18/04	1.469	1.493	1.02	1.00	0.04	PASS
	1.469	1.554	1.06	1.00	0.04	PASS
11/19/04	1.469	1.518	1.03	1.00	0.04	PASS
	1.469	1.481	1.01	1.00	0.04	PASS
11/24/04	1.440	1.394	0.97	1.00	0.04	PASS
	1.440	1.410	0.98	1.00	0.04	PASS
11/30/04	1.440	1.468	1.02	1.00	0.04	PASS
	1.440	1.491	1.04	1.00	0.04	PASS
12/02/04	1.430	1.419	0.99	1.00	0.04	PASS
	1.430	1.370	0.96	1.00	0.04	PASS
12/07/04	1.430	1.392	0.97	1.00	0.04	PASS
	1.430	1.344	0.94	1.00	0.04	PASS
12/08/04	1.430	1.363	0.95	1.00	0.04	PASS
	1.430	1.414	0.99	1.00	0.04	PASS
12/09/04	1.518	1.475	0.97	1.00	0.04	PASS
	1.518	1.504	0.99	1.00	0.04	PASS
12/13/04	1.518	1.500	0.99	1.00	0.04	PASS
	1.518	1.507	0.99	1.00	0.04	PASS
12/15/04	1.518	1.491	0.98	1.00	0.04	PASS
	1.508	1.519	1.01	1.00	0.04	PASS
12/17/04	1.472	1.476	1.00	1.00	0.03	PASS
	1.472	1.459	0.99	1.00	0.03	PASS
	1.472	1.440	0.98	1.00	0.03	PASS
12/22/03	1.502	1.490	0.99	1.00	0.03	PASS
	1.502	1.440	0.96	1.00	0.03	PASS
12/23/04	1.502	1.507	1.00	1.00	0.03	PASS
	1.502	1.486	0.99	1.00	0.03	PASS
12/30/04	1.450	1.417	0.98	1.00	0.03	PASS
	1.450	1.388	0.96	1.00	0.03	PASS

Figure 3. Typical Quality Control Standard Chart for Ethanol

DATE OF ANALYSIS	SAMPLE ID	RUN #1	RUN #2	% RPD	MAX. % RPD	STATUS
10/04/04	99 Caravan Ha2	0.569	0.556	2	100	PASS
11/17/04	38E1 dba	0.157	0.175	11	100	PASS
11/18/04	38E1 d1a	0.721	0.694	4	100	PASS
11/19/04	38E1 d2a	1.2	1.205	0	30	PASS
11/24/04	168E1 h1a	0.166	0.141	16	100	PASS
11/30/04	170E1 h1a	0.175	0.161	8	100	PASS
12/02/04	170E1 d1a	2.105	2.096	0	20	PASS
12/07/04	173E1 h1a	0.153	0.157	3	100	PASS
12/08/04	173E1 dba	0.131	0.126	4	100	PASS
12/09/04	173E1 d1a	1.227	1.136	8	30	PASS
12/13/04	177E1 d1a	0.726	0.671	8	100	PASS
12/15/04	178E1 H1a	0.155	0.162	4	100	PASS
12/17/04	178E1 D1a	0.79	0.763	3	100	PASS
12/22/04	181E1 H1A	0.119	0.101	16	100	PASS
12/13/04	1.5ppm	1.637	1.664	2	30	PASS
12/30/04	181E1 d1b	0.086	0.064	29	<L	PASS

Figure 4. Duplicate Control Chart for Methanol



Concentration	Area Counts
0.1033	402
0.1033	421
0.1033	464
0.1033	514
0.1033	396
0.1033	508
0.1033	487
0.5127	2535
0.5127	2415
0.5127	2354
1.0267	5034
1.0267	5314
1.0267	5297
1.5370	7729
1.5370	8029
1.5370	8061
3.0414	16515
3.0414	15959
3.0414	16461
10.2598	56128
10.2598	56381
10.2598	56060

slope	5499.0	
t	3.1	
r^2	0.9999	
std dev	49.7	
lod (t*s/m)	0.028	ug/mL

Figure 5. LOD Determination for Ethanol